

Application of First Principle Nickel System Battery Models to Aerospace Situations

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ABSTRACT

Battery models based on first principles have been under development for the last five to ten years. More recently, the appearance of faster and more sophisticated computational techniques, has allowed significant advances in the field. The usual approach consists of selecting the critical physicochemical phenomena of the given system (chemistry, mass transfer, charge transfer, etc.), setting up the problem as a set of coupled differential equations and obtaining numerical solutions. This approach was successfully implemented for the Pb-Acid system and subsequently for the NiCd system, at the cell level, by Prof. Ralph White of Texas A&M University. This NiCd cell model served as the basis of the NiCd Aerospace Battery model developed at JPL and reported at previous IECFC meetings.

At this time several aerospace battery models using the same approach are under development at JPL. The recent models are based on NiH₂ and NiMH chemistries. The current set of models uses a simplified treatment of the electrodes, this treatment assumes planar (non porous) electrode geometry. The resulting models have very modest computational requirements, allowing them to operate on personal computers. Results of performance predictions and computational requirements for the new models are discussed below.

1.0 INTRODUCTION

Mathematical models are being developed at the Jet Propulsion Laboratory for aerospace nickel batteries, i.e., nickel cadmium, nickel hydrogen and nickel metal hydride systems. The building blocks for these battery models are the first principle cell models developed at Texas A&M University and more recently at the University of

South Carolina. Macrohomogeneous approach has been adopted to describe the behavior of the porous electrodes in these models. Various physicochemical phenomena addressed in the cell models include: 1) material balance for the dissolved species generated/consumed by the electrochemical reaction and transported by diffusion and migration, 2) variations in the electrode porosity due to differences in the molar volume of the reactant and products, 3) changes in the electrochemical potential in the solid phase or in the electrolyte, 4) charge transfer kinetics, 5) principles of conservation of charge in the electrochemical cell, 6) effects of intercalation and slow diffusion of protons into the nickel oxide electrode and 7) changes in the electronic conductivity of the Ni oxide electrode during charge/discharge. The governing equations for the above phenomena are a set of coupled differential equations. These equations are solved for each of the regions (positive electrode, separator and negative electrode) with appropriate boundary and initial conditions by numerical methods. These methods are the Pentadiagonal (or Tridiagonal) BAND J method^(8,9) or Gear's method of lines⁽¹⁰⁾.

The above porous electrode models are certainly elegant and reveal the importance of transport limitations in the electrolyte phase. However, it seemed from the simulations that the mass transfer processes in the electrolyte phase have little effect on the electrode behavior. The charge discharge behavior of the Ni oxide electrode is essentially under "kinetic" control. Additionally, the porous electrode models have rather sophisticated computational requirements.

2.0 PLANAR APPROACH

Since the processes occurring across the surface film of active material, i.e., the changes in the electronic conductivity and in the proton concentration gradient across the film, and the charge transfer kinetics at the film-covered

regions, determine the charge discharge behavior of the Ni oxide electrode, a planar geometry with a thin uniform surface layer of active material should adequately represent the charge - discharge behavior of the Ni electrode. Approximating the porous electrode into a planar configuration should lead to substantial simplification of the mathematical operations in the model. This approximation is expectedly valid under normal cell operating conditions. At high rates, however, the transport processes in the electrolyte may not be neglected. The corresponding one-dimensional diffusion equations for the proton concentration across the surface film is solved analytically and incorporated into a discharge model, which also accounts for variable electronic conductivity across the film and charge transfer resistance at the film / electrolyte interface⁽¹¹⁾. This simplified approach provides fairly accurate predictions similar to the porous electrode models, as evident from our comparisons of the simulations from the simplified, planar model and the porous model. The planar model requires rather modest computational needs and can be ported on a personal computer. Additionally, it can be used as a model test bed to implement and verify any changes in the treatments of the electrochemical processes in the cell. Such changes, if required can later be transported on to the detailed porous models,

Using the above planar representation of the electrodes, various models have been developed for the Ni-based systems. In particular nickel-cadmium and nickel-hydrogen models have been developed at useable cell/battery level, with the required sub-routines, such as translator routine and charge definition routine. The translator routine converts the engineering level, design related parameters such as cell weight, volume, capacity, void volume, quantity of electrolyte, state of charge, precharge etc., to the dimensionless number employed in the model⁽¹²⁾. It enables the user to feed into the model all the design parameters characteristic of the cell, the performance of which is to be simulated. The charge definition routine consists of a series of charge discharge steps to simulate any power system architecture. The main features include multiple regime definitions with multiple control modes. Switching between regimes can be achieved by a range of triggering modes. Examples of regimes simulated include constant or

intermittent pulse discharges, constant current or constant potential (temperature compensated as in V_1) charges, or the more complicated LEO (Low Earth Orbit) or GEO (Geosynchronous Orbit) cycles.

3.0 Planar Model Simulations

Figure 1 shows the simulation of the constant current discharge curves of a 50 Ah Ni-Cd Cell from the planar as well as the porous model compared against the experimental data. As evident from the figure, there is a reasonably good agreement between the two predictions.

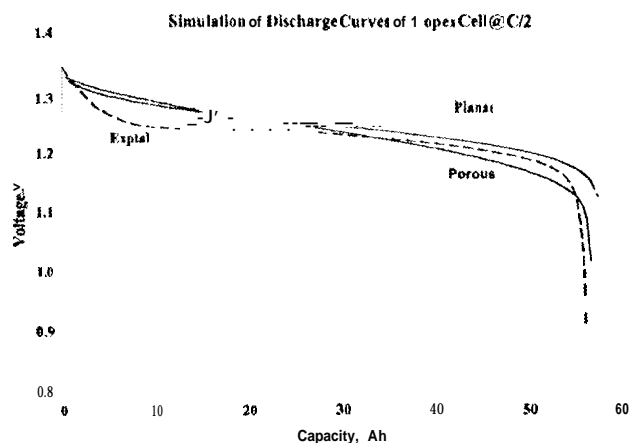


Fig. 1. Simulation of 50 Ah NiCd constant current discharge.

Both the predictions, however, differ from the experimental discharge curve, especially with respect to the profile in the first 25 % of discharge. The experimental curve appears sloping, whereas the simulations are fairly flat. This divergence is more prominent in the LEO cycles, where the discharge curves become more sloping during cycling (Fig. 2). This is attributed to the onset of a new phase of active material on the Ni electrode, which is discussed later on. The agreement in the simulations between the planar and porous models is an important consideration for pursuing the planar approach. A more detailed study to evaluate the planar model in comparison to the porous model is underway, to identify the limits within which the assumption of planar representation is valid.

Effect of 100 Cycles on Positive Potentials

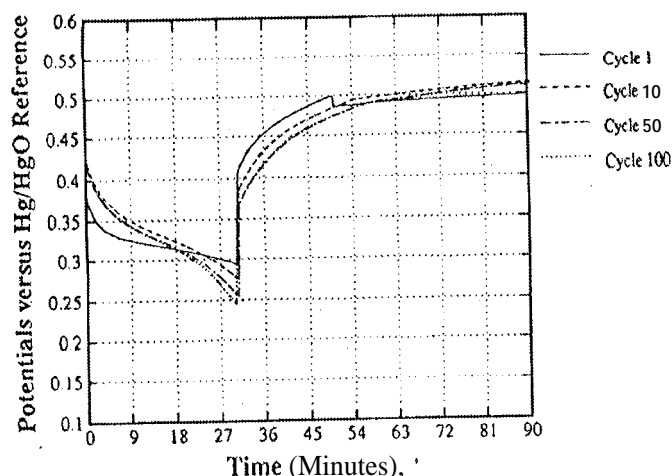
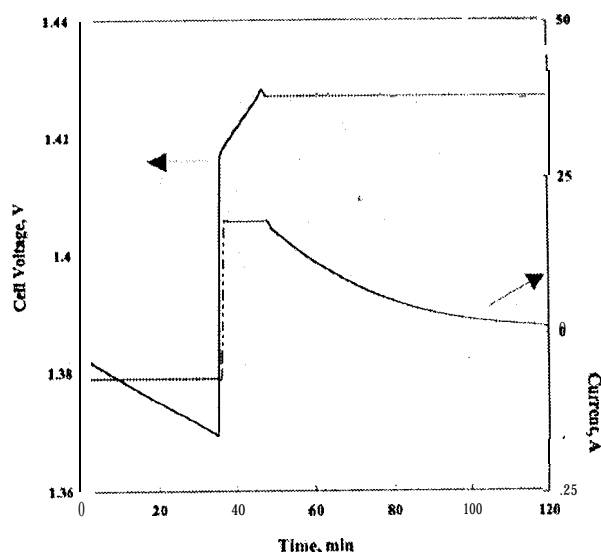


Fig. 2. Experimental boilerplate data for positive electrode.

In order to test the model under more intricate cyclic regimes, simulations have been made for LEO cycles typical of spacecraft applications. The cycle involves a discharge phase of 33 minutes, followed by charge at constant current to a specified voltage or V_1 level followed by a switch-over to a lapcrd-current mode. Fig. 3 illustrates the profiles of the voltage and current of a Ni-H₂ cell during a LEO simulation. One of the problems encountered with the porous models in such simulations is the instability of the models at the point switch-over.

Simulation of the Performance of a Ni-H₂ Cell under LEO Regime



Overshoots in voltage are often observed, mainly due to a constraint of the time-step for the numerical solution. In the planar models containing an analytical solution for the proton concentration, such overshoots are absent. In order to further demonstrate the applicability of this model to an application involving multiple pulsing steps, simulations have been carried out under SFUDS (Simulated Urban Federal Driving Schedule) routine for electric vehicles as depicted in Fig. 4. As may be seen from the figure, the cell voltage is stable with no undershoots or overshoots even in such an intricate schedule.

Predicted Ni-Cd Cell Voltage During SFUDS Cycle

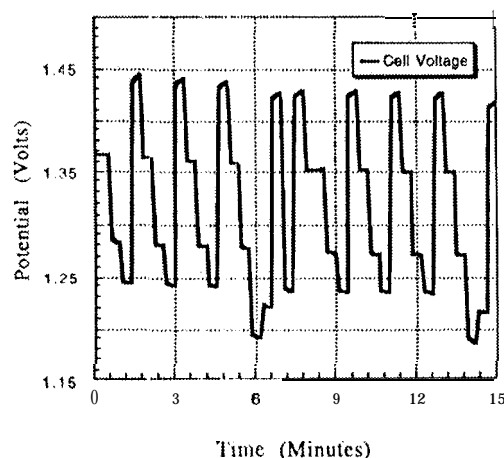


Fig. 4. Simulation of SFUDS cycle.

Finally, to demonstrate the use of the planar model as a test bed to implement changes in the description of electrochemical processes, the familiar multiple reaction scheme of the Ni oxide reaction has been treated by this approach to account for the sloping discharge profiles in the initial stages of discharge. It is well known that the NiOOH/Ni(OH)₂ can exist in multiple phases. On extended overcharge as in a spacecraft, the stable α -phase will transform into electrolyte-species-intercalated γ -phase, which reduces to β -Ni(OH)₂ on reduction. The existence of these multiple phases, occurring during cycling, will alter the discharge profile, as evident from the behavior of spacecraft batteries and boiler plate cells in a LEO regime. The above phases have been included in the planar Ni-Cd model, thus treating three simultaneous processes at the positive electrode, i.e., reaction of the β and

gamma phases and of oxygen. Assigning marginally different values for the charge transfer and diffusional kinetics and with different reversible potentials, i.e., 0.44 and 0.39 V vs. Hg/HgO , for the beta and gamma phases respectively, we could demonstrate the successive reduction/oxidation of the alpha-gamma and beta-beta phases, resulting in a sloping discharge curve at high states of charge. With this improvement, we have been able to simulate the changes in the discharge profiles during LEO cycling (Fig. 6)⁽¹³⁾. Efforts are currently underway to achieve similar improvements in the charge process. These improvements will be eventually carried over to the porous model also.

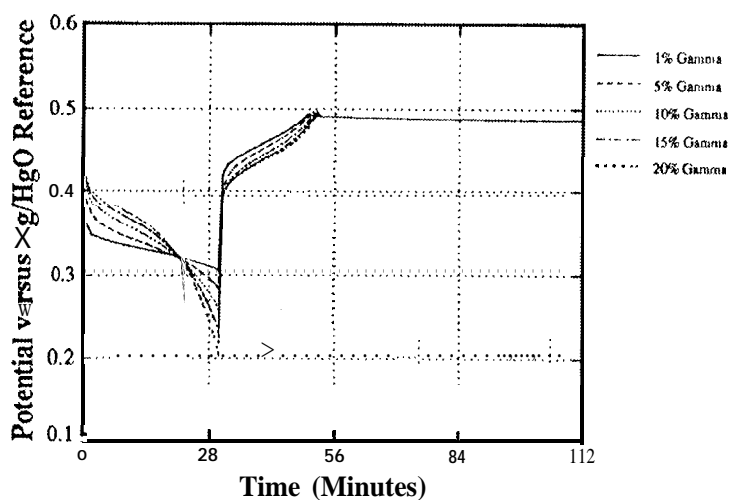


Fig. 5. Simulation of incorporation of two phase positive active material

4.0 CONCLUSIONS

Mathematical models for aerospace nickel-cadmium and nickel-hydrogen cells/batteries were developed based on the assumption that the discharge behavior of the Ni oxide electrode is predominantly controlled by the processes occurring at the surface film of Ni oxide such that the transport processes in the liquid phase can be ignored. This simplification, combined with an analytical solution for the proton concentration across the Ni oxide film provides a mathematical model of acceptable quality in predictions and in a PC-portable version. This model is fairly robust during complicated test regimes involving rapid current transients. Finally, this model can be used

as a test bed to implement changes and to verify modeling of new processes, as demonstrated by the inclusion of an additional phase of Ni oxide to improve the accuracy of predictions.

5.0 ACKNOWLEDGMENTS

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